Int J Ind Chem (2016) 7:103–108
DOI 10.1007/s40090-015-0058-4

RESEARCH

Fabrication and characterization of grafted polymer electrode self modification with activated carbon

Muhammed Mizher Radhi[1]

Received: 12 June 2015 / Accepted: 24 September 2015 / Published online: 18 November 2015

Abstract A new grafted polymer electrode self modified with activated carbon (GPESMAC) was fabricated and electrochemical characterization by cyclic voltammetric analysis. The polystyrene was used as polymer grafted with acrylonitrile as a monomer and activated carbon as improvement material using gamma irradiation to produce a new copolymer. The redox process of $K_3Fe(CN)_6$ during cyclic voltammetry was studied with the new working electrode (GPESMAC) by cyclic voltammetric analysis. The physical properties of these electrodes have high hardness, insolubility, and stability at different high temperatures. Also, the sensitivity under conditions of cyclic voltammetry is significantly dependent on different scan rate and concentrations. The GPESMAC was characterized by surface analytical methods including SEM and AFM. Interestingly, the redox reaction of Fe(III) solution using GPESMAC remained constant even after 15 cycles. It is therefore evident that the GPESMAC possesses some degree of stability. The potential use of the grafted polymer as a useful electrode material is therefore clearly evident. It is through the study of applications in quantitative and qualitative analysis proved that the conductivity of grafted polymer with activated carbon is highly efficient and stability compared with the commercial solid electrodes and modified by mechanical means or by evaporating the solvent, such as glassy carbon electrode. On the other hand an enhancement of redox current peaks and high detection limits effective species such as Fe(II)/Fe(III) was studied.

✉ Muhammed Mizher Radhi
mmradhi@yahoo.com

[1] Health and Medical Technology College, Middle Technical University, Baghdad, Iraq

Keywords Grafted polymer electrode self modified · Activated carbon · Redox couple Fe(III)/Fe(II) · Electrocatalysis · Cyclic voltammetry

Introduction

The process of modifying polymers with good conductive materials stirs the attention of the scientists in recent times. One of these methods is irradiation of grafting polymers and modified with conductive materials to be used for multiple purposes, especially in the field of conductors and semiconductors, as well as in electrochemistry [1–4].

A composite polymer membrane working electrode has been studied at cyclic voltammetric for famotidin and terthiophene determination of drug in pharmaceutical formulation. This composite film of polymer electrode showed good catalytic behavior, which includes a good current response [5, 6].

The modified electrode functionalized with polyacrylic acid (PAA) tethered to indium tin oxide (ITO) and covered with gold nanoparticle (ITO/PAA/Au) demonstrated switchable interfacial properties discriminating different pH. The switchable electrochemical and plasmonic process was characterized by cyclic voltammetry (CV), electrochemistry impedance spectroscopy (EIS), and localized surface plasmon resonance (LSPR) [7].

Grafted molecularly imprinted (MIP) polymer thin films onto Au electrodes was studied as good sensor in the presence of *N*,*N*′-methylenebis(acrylamide) to detection of hydroquinone [8].

Another study for using a molecularly imprinted polymer (MIP) as a recognition element in the development of a heparin sensor for real-time monitoring. An indium tin oxide (ITO) electrode grafted with a heparin-specific MIP was used

as a working electrode to perform cyclic voltammetry of ferrocyanide. The anodic current was found to be dependent on heparin concentration. Therefore, the MIP-grafted electrode is suitable for real-time monitoring of heparin in blood. The advantage of these method is that a very small volume of blood is needed, which is very important, especially when regular measurements are required [9].

The electrical connectivity of grafted polymer with pair of electrons located on the nitrogen atom within the structure of grafted polymer, and in addition to that the presence of high conductivity in a series of a activated carbon is one of the reasons used in the manufacture of electrodes operating polymeric high connectivity characteristic, which is mainly used in the analysis electrochemistry, especially in a cyclic voltammetry [4].

One of the syntheses of grafting polymers is electropolymerization of statistically exposed dithiobenzoate moieties served as a chain transfer agent for the polymerization of styrene on a matrix of an electrodeposited conjugated polymer. The polystyrene modified substrate was then used as the macro chain transfer agent for the synthesis of the second block of poly-tert-butyl acrylate on the surface. The polymerization from the surface was characterized by surface analytical methods including AFM, XPS, and contact angle measurements [10–14].

In this work, grafted polymer was modified with activated carbon to fabrication grafted polymer electrode self modified with activated carbon by gamma ray. The new grafted polymer electrode was electrochemically characterized in $K_3Fe(CN)_6$ with KCl aqueous electrolyte by CV technique.

Experimental

Synthesis of grafted polymer modified with activated carbon (GP/AC)

Polystyrene-acrylonitrile was grafted with activated carbon (AC) as an improvement material, using gamma-irradiation. The new grafted polymer modified with activated carbon indicated that the best grafting percentage ratio could be revealed when the concentration of the catalyst ferrous ammonium sulphate (FAS) is about 2 % and the monomer concentration is 90 %, at gamma ray dose 1.25 M rad [4].

Instrument and electroanalytical methods

Electrochemical workstations of NuVant Systems Inc., USA (EZ stat series with potentiostat/glvanostat driven by electroanalytical measuring software) were connected to a PC computer in order to perform cyclic voltammetry (CV), chronoamperometry (CC), and chronoamperometry (CA). An Ag/AgCl (3 M NaCl) and platinum wire (1 mm diameter) were used as the reference and counter electrodes, respectively.

Grafted polymer electrode self modified with AC was used as a working electrode in this study. The voltammetric experiments were carried out with 0.1 M KCl as supporting electrolyte and using $K_3Fe(CN)_6$ solution for calibration. The solution was degassed with nitrogen gas for 10–15 min prior to recording the voltammogram.

Reagents

All reagents were analytical reagents or electrochemical grade purity. All solutions were prepared using double distilled water. Unless otherwise specified, the supporting electrolyte was used 0.1 M KCl in aqueous media at room temperature.

Fabrication of grafted polymer electrode self modified with activated carbon (GPESMAC)

GPESMAC has been fabricated from grafted polymer modified with activated carbon. The diameter of electrode was 3 cm. A (1 mm) hole was made in the grafted polymer to allow 1 cm length of platinum wire out from the other side of electrode. A copper wire was then joined with the platinum wire. After that, all parts of fabricated electrode were covered with glassy tube and then fixed with epoxy resin.

Results and discussion

Electrochemical properties of grafted polymer electrode self modified with activated carbon (GPESMAC)

Potential window of GPESMAC

0.1 M of potassium chloride solution is commonly used as a reference standard for the purpose of calibrating a voltammetric system in aqueous solutions. During the calibration process of the electroanalytical workstation using GPESMAC as a working electrode, comparison with the working potential window of GCE/AC (using attachment method for modification GCE with AC) was found to be in the range (−1.8 to +1.8 V) with large value of capacity as show in Fig. 1a with small significant peaks appearing at +1.4 V. A considerable extension of the working window with the absence of each, especially at the anodic region, is observed when GPESMAC is used. Although the working window at the anodic and cathodic

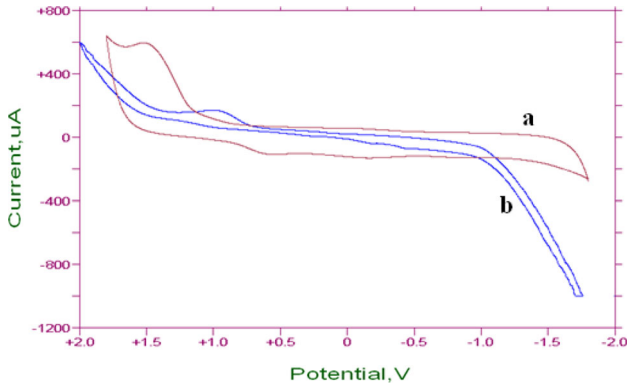


Fig. 1 Cyclic voltammetry of different electrodes **a** glassy carbon electrode modified with activated carbon by mechanical attachmemt method, **b** grafted polymer electrode self modified with activated carbon in 0.1 M KCl as supporting electrolyte versus Ag/AgCl and 100 mV s^{-1}

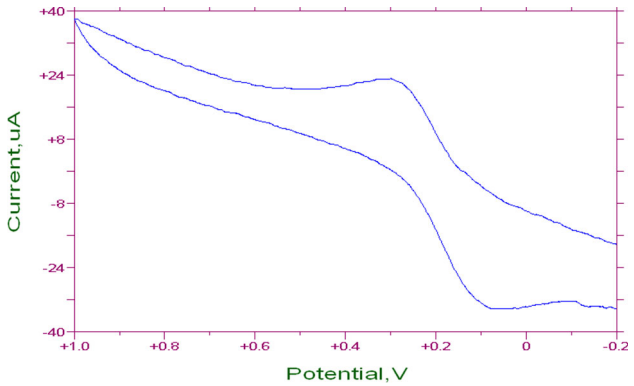


Fig. 2 Cyclic voltammetry of GPESMAC in 1 mM $K_3Fe(CN)_6$ with 0.1 M KCl as supporting electrolyte versus Ag/AgCl and 100 mV s^{-1}

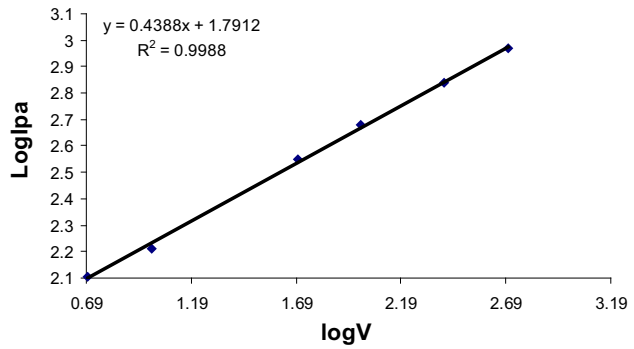


Fig. 3 Plot log Ipa (anodic current) versus log (scan rate) of GPESMAC in 0.1 M KCl and 1 mM $K_3Fe(CN)_6$ versus Ag/AgCl and scan rate 5–500 mVs^{-1}

regions deteriorates, this is due to the ''electrocatalyzed'' oxidation–reduction of the aqueous electrolyte or the reactivity of GPESMAC giving rise to a limiting current

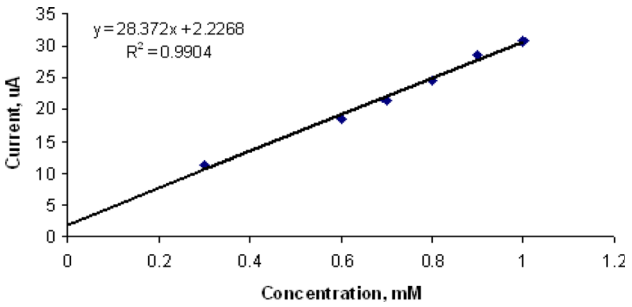


Fig. 4 Plot Ipc(cathodic current) versus different concentration $K_3[Fe(CN)_6]$ (0.3–1 mM) in 0.1 M KCl at scan rate 100 mV s^{-1} using GPESMAC versus Ag/AgCl

appearing at about −1.5 to +2.0 V with low capacity as show in Fig. 1b. This limiting current, however, diminishes in subsequent cycles allowing the potential working window to be widened at the anodic region to near 2.0 V.

Effect of GPESMAC on the redox reaction of $K_3[Fe(CN)_6]$ during CV

It was found that the redox potential of GPESMAC in 1 mM $K_3Fe(CN)_6$ with 0.1 M KCl as supporting electrolyte with anodic and cathodic potential peaks as shown in Fig. 2:

$$\text{Epa} = +200\ \text{mV}(\text{oxidation potential of anodic peak})$$

$$\text{Epc} = +100\ \text{mV}(\text{reduction potential of cathodic peak})$$

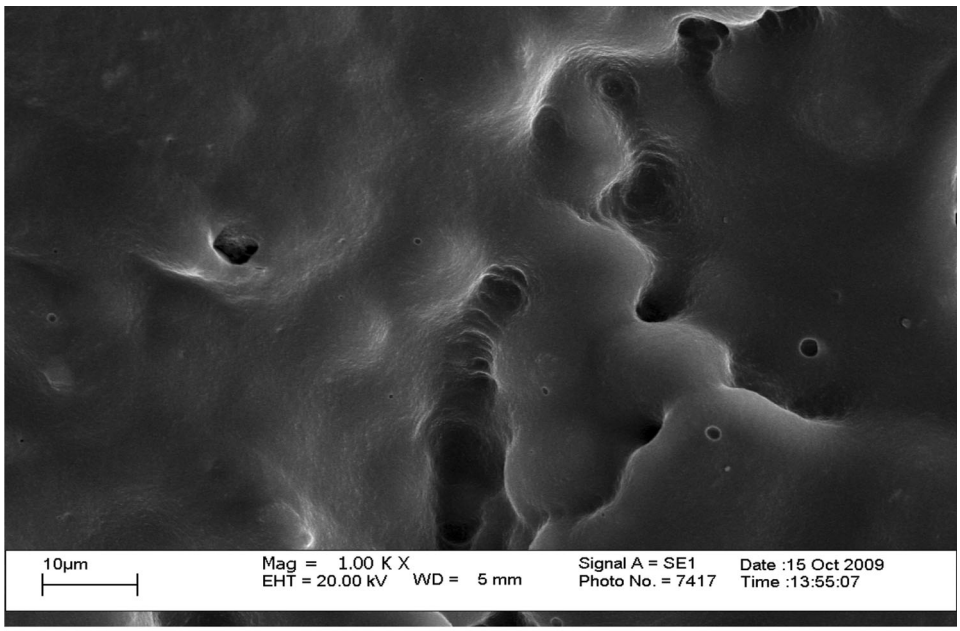
with peak separation of 100 mV (for $n = 1$) in 0.1 M KCl electrolyte indicates the reversible reaction of the Fe(III)/Fe(II) couples in KCl solution, and agrees well with the accepted values.

Effect of varying scan rate

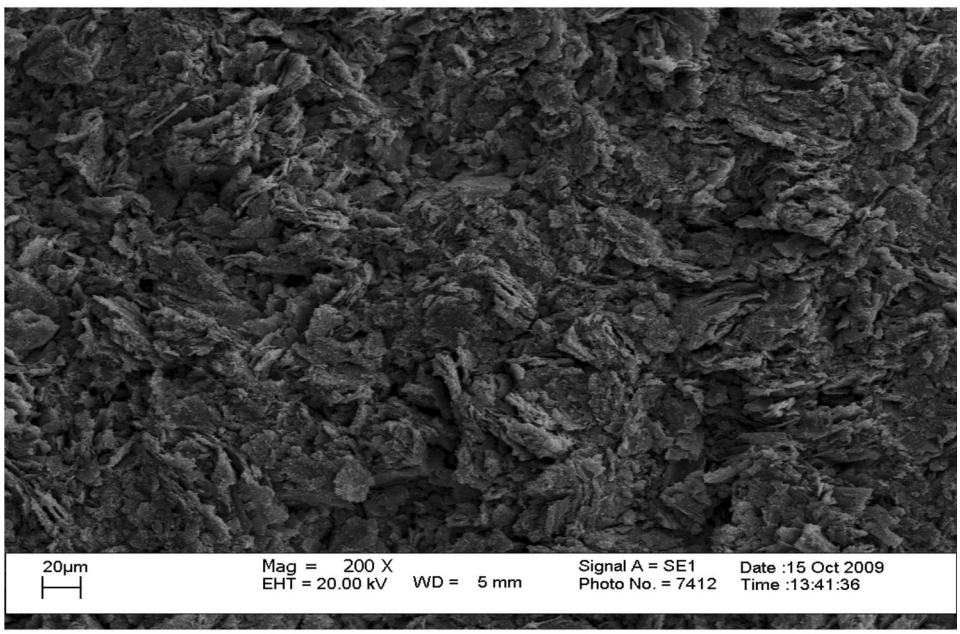
The effect of varying scan rates on the cyclic voltammograms using GPESMAC as working electrode in 0.1 M KCl supporting electrolyte was studied with 1 mM $K_3Fe(CN)_6$ over a scan rate range of 5–500 mV s^{-1}. Oxidation and reduction currents of the Fe(III)/Fe(II) couple was observed to increase with scan rate due to heterogeneous kinetics and IR effect. Based on a plot of log(Ipa) versus log (scan rate) for the oxidation current of the first cycle, a straight line was obtained in Fig. 3 fulfilling the equation: $y = 0.4388\ X + 1.7912$ with $R^2 = 0.9988$. A slope of 0.44 is quite comparable with the theoretical slope of 0.5 for the diffusion controlled process.

Effect of varying temperature

Effect of temperature on the redox process of $K_3Fe(CN)_6$ was studied on GPESMAC. The current increases gradually



(a)



(b)

Fig. 5 SEM of **a** grafted polymer, **b** grafted polymer modified with CNT

at a temperature of 10–90 °C. Plots of log (Ia) oxidation current of $K_3Fe(CN)_6$ versus the reciprocal of temperature, which is found to be fairly linear in agreement with the thermodynamic expectation of Arrhenius equations [15]:

$$\sigma = \sigma^{\circ}\mathrm{Exp}\ (-\ \mathrm{Ea}/\ RT\ ) \quad (1)$$

$$D\ =\ D^{\circ}\mathrm{Exp}\ (-\mathrm{Ea}/\ RT) \quad (2)$$

where: σ/D are conductivity/diffusibility and σ°/D° are standard conductivity/the initial diffusibility.

From the relationship between log(Ia) and $1/T$ of the oxidation $K_3Fe(CN)_6$ as Fe(II)/Fe(III) the activation energy was found 6.32 kJ/mol in GPESMAC comparison with other studies [16].

Effect of varying $K_3Fe(CN)_6$ concentration

Figure 4 shows the linear current dependent on $K_3Fe(CN)_6$ concentration; observed at concentration range (5–10 mM) which is described by the equation of $y = 28.372X + 2.2268$ with $R^2 = 0.9904$. The slope of the linear line for $K_3Fe(CN)_6$ showed that a considerably high

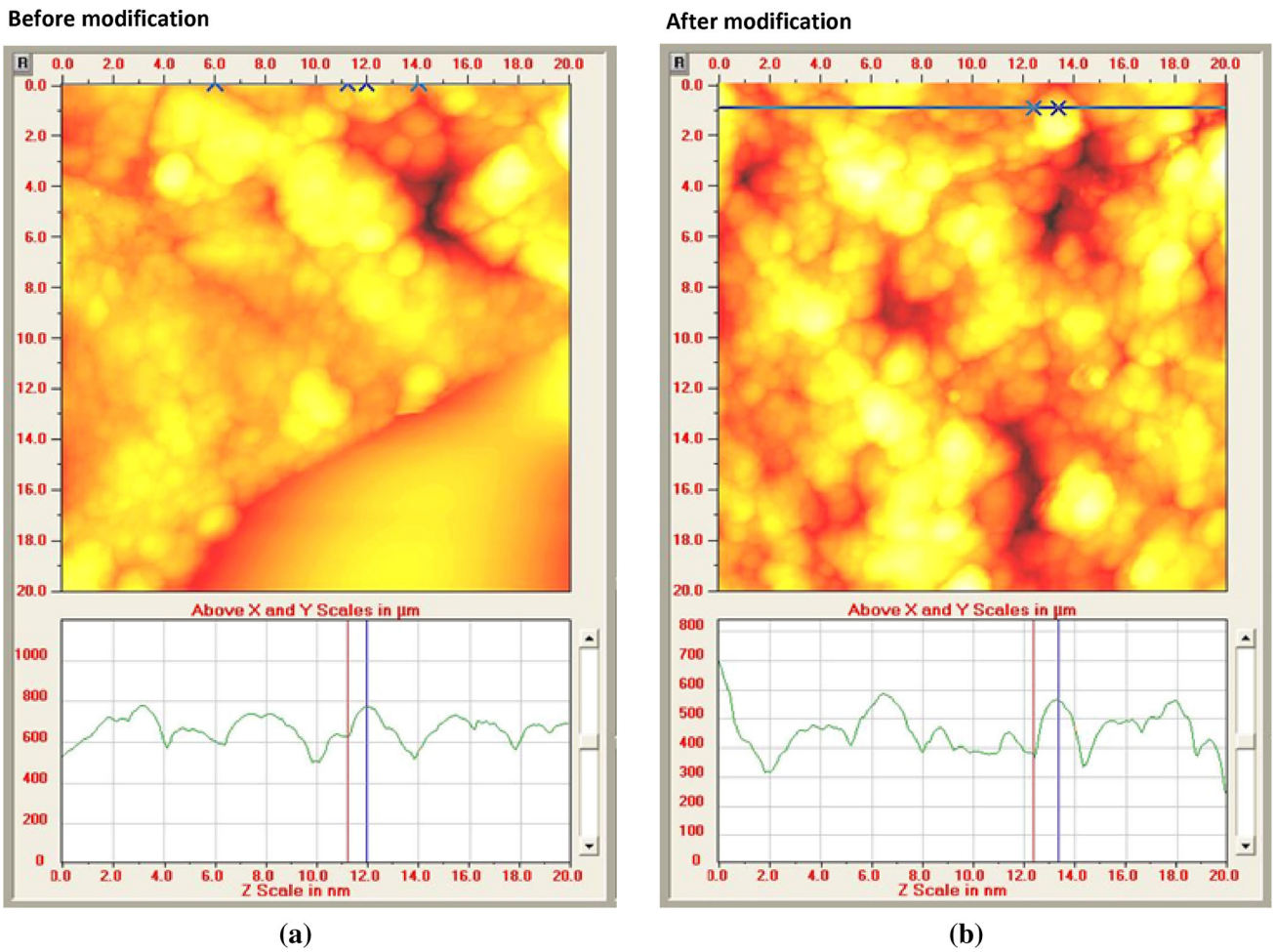


Fig. 6 AFM of grafted acrylonitrile on polystyrene **a** before modified with activated carbon, **b** after modification

sensitivity response of 28 µA/mM is readily obtained at GPESMAC during cyclic voltammetry.

Reproducibility

The potential cycling of the redox of GPESMAC in 1 mM $K_4Fe(CN)_6$ and 1 M KCl aqueous solution as a supporting electrolyte was carried out during cyclic voltammetry. Continuous potential cycling did not seem to affect the redox current of GPESMAC as the faradic activity appears reproducible even after 15 cycles, reflecting the stability and reproducibility at the surface of GPESMAC.

Scanning electron microscopy (SEM) of GPE/AC

Before modification grafted polymer surface appears compact and nonporous. The uniformity of the grafted polymer surface slightly increases since occurrence of protrusion observed phase as shown in Fig. 5a. After modification with AC, although many of the species deposits with homogenous distribution of AC still remain at about <1 µm as show in Fig. 5b.

Atomic force microscopy (AFM)

The surface image of AFM in an area of 20 µm × 20 µm of the grafted polymer (polystyrene acrylonitrile) before and after modified with AC as shown in Fig. 6a, b respectively. The surface of the electrode appeared to be compact and rough. According to AFM images, the average species size and thickness of the film were estimated to be 11.23 and 28.69 µm, respectively.

Conclusion

A grafted polymer electrode self modified with activated carbon GPESMAC has been fabricated in laboratory for using in cyclic voltammetric technique as a working

electrode. The new electrode was used as alternative of working electrodes modified with deposit materials such as activated carbon using classical modification methods (attachment or solvent evaporation methods). The CV analysis results of these electrodes have an extended potential working region as compared to the routine modification method of GCE with activated carbon and have high stability and reproducibility. Redox peaks of Fe(II)/Fe(III) showed high current as compared with other modified electrodes.

Electro-catalytic activity of GPESMAC is therefore evident in this study, it was studied by redox process of $K_3Fe(CN)_6$ during cyclic voltammetry. The redox peaks potential shifts slightly to less negative value by about 100 mV for oxidative peak and 50 mV for reductive peak with current enhancement of about 3-fivefolds. The sensitivity under conditions of cyclic voltammetry is significantly dependent on the concentration, scan rate and temperature. Excellent reproducibility and stability of the current is observed, provided a fabricated electrode is used for each experiment without any polishing.

References

1. Bhattacharya A, Misra BN (2010) Grafting: a versatile means to modify polymers techniques, factors and applications. Prog Polym Sci 29:767–814
2. Radhi MM, Tan WT, Ab Rahman MZ, Kassim AB (2010) Voltammetric detection of Hg(II) at C60, activated carbon and MWCNT modified glassy carbon electrode. Res J Appli Sci 5:59–64
3. Radhi MM, Tan WT, Ab Rahman MZ, Kassim AB (2010) Electrochemical redox of Hg^{2+} mediated by activated carbon modified glassy carbon Electrode. Int J Electrochem Sci 5:615–629
4. Radhi MM, Tan WT, Rahman MZ, Kassim AB (2012) Synthesis and characterization of grafted acrylonitrile on polystyrene modified with activated carbon using gamma-irradiation. Sci Res Ess 7:790–795
5. Radhi MM, Al-Mulla EAJ (2015) Use of a grafted polymer electrode to study mercury ions by cyclic voltammetry. Res Chem Intermed 41:1413–1420
6. Tan WT, Radhi MM, Ab Rahman MZ, Kassim AB (2011) Application studies to voltammetric detection of trace Hg(II) by different modified solid glassy carbon electrode. Austr J Basic Appli Sci 5:2475–2481
7. Abdullah AA, Aowda SA (2013) Electrochemical studies of copper fatty amides complex in organic medium. Res Chem Intermed 39:2817–2823
8. Yunus WMZ, Ibrahim NAB, Rahman MZA (2010) Epoxidized palm oil plasticized polylactic acid/fatty nitrogen compound modified clay nanocomposites: preparation and characterization. Polym Polym Comp 18:451–459
9. Radhi MM, Al-Mulla EAJ (2014) Application study of grafted polymer electrode in manganese ions during cyclic voltammetry. Rend Lincei Sci Fis Nat 25:209–213
10. Shemmari FA, Rabah AA (2014) A comparative study of different surfactants for natural rubber clay nanocomposite preparation. Rend Lincei Sci Fis Nat 25:409–413
11. Al-Mulla EAJ (2011) Lipase-catalyzed synthesis of fattythioic acids from palm oil. J Oleo Sci 60:41–45
12. Yunus WMZ, Ibrahim NAB, Rahman MZA (2010) Difatty acyl urea from corn oil: synthesis and characterization. J Oleo Sci 59:157–160
13. Al-Mulla EAJ (2011) Preparation of polylactic acid/epoxidized palm oil/fatty nitrogen compounds modified clay nanocomposites by melt blending. Polym Sci Series A 53:149–157
14. Issam AM, Al-Janabi KW (2015) A novel method for the synthesis of biodiesel from soybean oil and urea. C R Chim 18:525–529
15. Tan WT, Lim E, Bond A (2003) Voltammetric studies on microcrystalline C60 adhered to an electrode surface by solvent casting and mechanical transfer methods. J Solid State Electrochem 7:134–140
16. Radhi MM, Al-Mulla EAJ, Tan WT (2014) Electrochemical characterization of the redox couple of Fe(III)/Fe(II) mediated by grafted polymer electrode. J Res Chem Intermed 40:179–192